# Microscale Preparation of Tin (IV) Iodide[1]

## Introduction

Like the transition metals, many of the heavier main-group elements exhibit more than one oxidation state. An example of this occurs with the element tin (Sn), which has two common oxidation states: Sn(IV) (commonly named stannic) and Sn(II) (commonly named stannous). Both have approximately equal stability. In contrast, the lighter Group 14 (IVA) elements, carbon, silicon, and germanium, are nearly always found in the +4 oxidation state. Lead, however, is most often found in the +2 state, with the +4 state being fairly unstable. Thus, tin occupies an intermediate position in the group trend towards higher stability for the Pb(II) oxidation state. This kind of trend is found in the other main group families in the p-block [Groups 13 – 16 (IIIA - VIA)], where the primary oxidation number decreases by two going down the group. This phenomenon is known as the *inert pair effect*, referring to the tendency to retain a configuration $ns^2$ for bonded atoms of the heavier members of the group.[2]

The trend can be rationalized in the following way, using Group 14 (IVA) elements as examples. The electronic configuration of the family is $ns^2np^2$, with the electrons being arranged as follows:

$$\underset{ns}{\underline{\upharpoonleft\downharpoonright}} \quad \underset{np}{\underline{\upharpoonleft}\ \underline{\upharpoonleft}}$$

In this electronic state the element can form two covalent bonds, using two unpaired electrons in the *np* subshell. The two electrons in the *ns* orbital, which are not used to form bonds in this case, are sometimes termed an *inert pair*. This type of bonding is seen with Sn(II) and Pb(II). Alternately, the *s* electrons can be promoted to the empty *p* orbital at the cost of an absorption of energy by the element, resulting in the following electronic arrangement.

$$\underset{ns}{\underline{\upharpoonleft}} \quad \underset{np}{\underline{\upharpoonleft}\ \underline{\upharpoonleft}\ \underline{\upharpoonleft}}$$

Four equivalent covalent $sp^3$ hybrid bonds can now be formed by the element. Bond formation occurs with release of energy; therefore, the energy required to achieve $sp^3$ hybridization is compensated by the bond energy. This type of bonding is seen with the +4 state of all the Group 14 elements, including Sn(IV) and Pb(IV). The likelihood of achieving the +4 state can be explained in terms of trends in two properties:

1. The ease of electron promotion, becoming easier for heavier members due to greater distance of the valence electrons from the nucleus.
2. Bond strength, being stronger for lighter members due to compact orbital size, short bond lengths, and good orbital overlap.

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[1] Adapted from Z. Szafran, R. M. Pike, and M. M. Singh, *Microscale Inorganic Chemistry*, John Wiley & Sons, New York, 1991.

[2] It should be pointed out that in all these cases we are not referring to true ionic charges on the elements, since the compounds are appreciably covalent.

In the cases of carbon, silicon, and germanium, the "cost" of electron promotion is more than compensated by the "return" of energy from the additional two bonds formed. These elements are thus found in the +4 oxidation state. In the case of tin, the sum of "cost" and "return" for bonding in the +4 state is comparable to that for the +2 state; hence, both states have approximately equal stability. In the case of lead, the "cost" of electron promotion is not compensated by the small return from the two additional bonds. Lead is therefore generally found in the +2 oxidation state, and compounds in which it has the +4 state are potent oxidizing agents, being readily reduced back to the more stable +2 state.

Sn(IV) compounds may be prepared by direct reaction of metallic tin with mild oxidizing agents, such as iodine. The iodine is consequently reduced from the elemental state (0) to the -1 state.

$$\mathrm{Sn} + 2\mathrm{I}_2 \rightarrow \mathrm{SnI}_4$$

The direct reaction results in formation of the slightly more stable +4 oxidation state. The stability advantage of the +4 state is not great, and some $\mathrm{SnI}_2$ is produced, as well. This is separated from the desired product by washing with methylene chloride.

In this experiment you will prepare $\mathrm{SnI}_4$ on a microscale. You will be using elemental iodine, which is harmful if swallowed, inhaled, or absorbed through the skin. It readily sublimes (vaporizes from the solid state) at atmospheric pressure, especially if warmed. It is a lachrymating agent (makes your eyes tear up). Methylene chloride (b.p. = 40 $^{o}$C), the solvent in this preparation, is also harmful if swallowed, inhaled, or absorbed through the skin. Exposure may cause nausea, dizziness, and headache. It is a narcotic at high concentrations and is a possible carcinogen. Exposure should be minimized.

## Procedure

Carry out all operations in a well ventilated fume hood. Place 119 mg (1.00 mmol) of tin and 475 mg (1.87 mmol) of iodine in a 10-mL round-bottom flask containing a stir bar and equipped with a reflux condenser, as shown in Fig. 1.

Add 6.0 mL of methylene chloride through the condenser using a Pasteur pipet. Gently heat the flask and contents using a hot plate until a *mild* reflux is maintained. This can be detected by a moderate dripping rate from the bottom of the condenser joint. Maintain the system at the reflux temperature until there is no visible violet color of iodine vapor in the condenser throat (~30-40 minutes).

Gravity filter the <u>warm</u> solution *rapidly* through a loose glass wool plug using a small glass funnel (hint: warm the glass funnel with glass wool in the oven prior to use). Collect the filtrate (liquid) in a 10-mL Erlenmeyer flask. Any unreacted tin

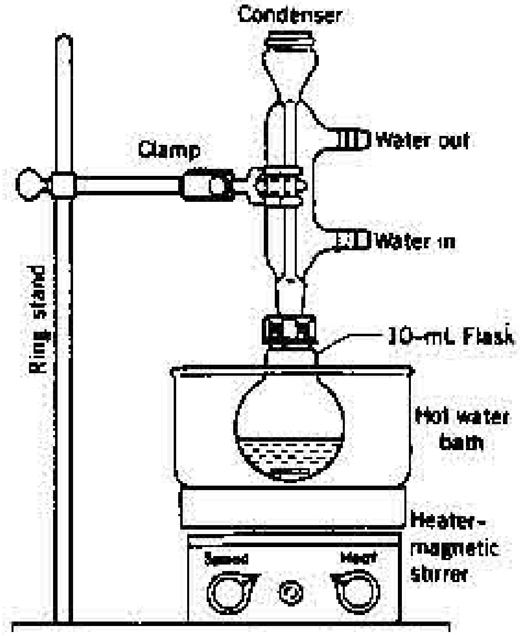

Figure 1

metal will remain in the funnel. Rinse the reaction flask with an additional 1 ml of warm methylene chloride, and also pass this solution through the filter, collecting the filtrate in the same flask. Add a boiling stone to the filtrate and concentrate the solution on a *warm* (not hot) hot plate to approximately 2 mL. Cool the resulting solution in an ice-water bath, and collect the orange-red crystals of tin(IV) iodide by suction filtration using a Hirsch funnel. Wash the solid with two 0.5-mL portions of cold methylene chloride, and dry the crystals on a filter paper. Determine the melting point of the product (m.p. = 144.5 $^{o}$C), and calculate the percent yield.

## Reactions of $SnI_4$

Dissolve a small amount of the product, $SnI_4$, in 5 mL of acetone. Divide this into two portions, A and B. To portion A, add a few drops of water. To portion B, add a few drops of saturated KI solution. Observe what happens in each case, and explain your observations in terms of the nature of the product.

## Laboratory Report

1. Submit your sample, clearly labeled with the names of all group members participating in the preparation.

2. Your written report should include a statement of milligrams of product and percent yield, the observed melting point, and a brief description of any unexpected results or departures from the procedure.

3. Describe your observations and interpretations, including balanced chemical equations, for the reactions you carried out with $SnI_4$, both with water and saturated KI solution.

4. Methylene chloride is a suitable solvent for this preparation because it effects the separation of $SnI_2$ from $SnI_4$. Explain in detail why this occurs (hint: start with VSEPR theory). Why would water or alcohol be a poor substitute?